Thermal Expansion of the Pentlandite Structure

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Abstract

Natural pentlandite has a smaller cell dimension than the synthetic pentlandite of identical composition and shows a nonreversible thermal expansion after heating at moderately low temperatures. The reasons for the irreversible expansion have not been completely understood. Therefore, structures of Frood pentlandite ($Fe_{3.97}Ni_{4.84}Co_{0.07}S_8$) and Outokumpu pentlandite ($Fe_{1.63}Ni_{1.82}Co_{5.6}S_8$) were refined using single-crystal X-ray intensity data collected at high temperature (200°C for Frood and 235°C and 350°C for Outokumpu) and at room temperature after heating. Refinements resulted in final unweighted R factors ranging from 0.019 to 0.033. Only Frood pentlandite showed "irreversible" thermal expansion (initial room temperature $a = 10.038$ Å and final room temperature [after heating] $a = 10.093$ Å). Also, the reversible component of the thermal expansion in Frood pentlandite is two times as large as that in Outokumpu pentlandite.

For the Frood pentlandite, the octahedral $M(O)$-S distance increased significantly after annealing (from 2.377 Å to 2.418 Å); however, the average $M(T)$-S distance did not change at all. This differential polyhedral expansion is interpreted as resulting from the disorder of iron and nickel between the two metal sites, leading to an enrichment of high-spin Fe^{2+} in the octahedral site relative to its occupancy in the natural mineral.

Introduction

Natural pentlandites [$(Fe, Ni, Co)_{9\pm x}S_8$] exhibit an interesting thermal expansion behavior. Knop, Ibrahim, and Sutarno (1965) observed that the a cell dimension of a natural pentlandite is smaller than that of synthetic pentlandite of identical composition. They also found that annealing of natural pentlandites at temperatures between 150° and 200° causes an increase in the cell edge which was irreversible with respect to cooling time (unspecified) for their experiments.

Annealing at argon pressures as high as 2000 atm prior to X-ray studies did not prevent this irreversible expansion. After annealing, the a cell edge became approximately equal to that of synthetic pentlandite of the same composition. Also notable is that synthetic pentlandite shows a large thermal expansion(though not an irreversible one), as much as 10 times that of ZnS over the same temperature interval (Kullerud, 1963; Morimoto and Kullerud, 1964). A knowledge of the reasons for the irreversible expansion of pentlandite should

be useful in understanding the crystal chemistry of sulfide minerals and the problem of pentlandite formation in nature.

At least four possibilities should be considered which might be responsible for the irreversible thermal expansion. These include: (1) dissolution of intergrown and/or exsolved phases such as pyrrhotite and mackinawite, (2) disordering of metal atoms between nonequivalent sites in the pentlandite structure, (3) magnetic changes, perhaps due to a change in the spin state of octahedral Fe, and (4) a change in the metal:sulfur ratio upon heating. Of these four, the first one was ruled out by Knop *et al* (1965, p. 311) on the basis that the observed increase in the cell edge would require an initial pentlandite/pyrrhotite ratio of approximately 8:7. Knop, Huang, and Woodhams (1970) tested the second possibility by studying Mössbauer spectra of powdered samples of pentlandite, obtained before and after annealing. They found that in untreated pentlandite (from Creighton Mine, Sudbury), high-spin Fe^{2+} was apparently enriched in the octahedral site; annealing resulted in the antiordering of iron and its enrichment in the tetrahedral sites. This antiordering was thought to be responsible

for the irreversible thermal expansion. Vaughan (1971) studied the Mössbauer spectrum of powdered samples of pentlandites from Worthington Mine, Sudbury, and also found an enrichment of iron in the octahedral site (though to a smaller extent than that observed by Knop *et al*). As to the third possibility, Vaughan and Burns (1971) suggested that the octahedral cobalt and iron in pentlandite could be in low-spin state. The observed expansion in pentlandite might be due to a change in the spin state [low-spin $(L \cdot S) \rightarrow$ high-spin $(H \cdot S)$] of octahedral iron.

Objectives of the Present Study

Because the present report is a continuation of our previous study on natural pentlandite (Rajamani and Prewitt, 1973), the reader is referred to this paper for a detailed discussion of the structure and chemistry of natural pentlandite. Briefly, the structure of pentlandite $(Fe, Ni, Co)_{9 \pm x}S_8$ is based on the pseudo cubic-closest-packing of sulfur atoms with cations occupying 1/8 of the available octahedral and 1/2 of the available tetrahedral holes in the sulfur framework. In the unit cell, there are 36 metal atoms distributed over 4 octahedral (4b) and 32 tetrahedral (32f) sites. These sites are designated as $M(O)$ and $M(T)$, respectively. Complete ordering of cations (iron and nickel in the common natural pentlandites) in the two non-equivalent metal sites would be expected only when the Fe:Ni ratio is either 1:8 or 8:1. These compositions have not been observed to be stable in the synthetic system (Knop and Ibrahim, 1961), nor have these compositions been found in nature (Knop *et al*, 1965). Though Fe:Ni ratios in pentlandite vary widely, they usually fall within a small range, approximately between 3:1 and 1:3 (Knop and Ibrahim, 1961). Therefore, even if the octahedral site is completely occupied with one kind of atom, the tetrahedral sites will always contain both kinds of atoms.

The observed enrichment of iron in the octahedral sites of natural pentlandite is surprising in view of the fact that Ni^{2+} invariably shows a very high preference for the octahedral sites in many crystal structures because of its high octahedral site preference energy (Burns, 1970). For example, the estimated octahedral site preference energy for Ni^{2+} in oxide spinel structures is 20.6 kcal/mole, whereas for Fe^{2+} it is only 4.0 kcal/mole (Burns, 1970). Cation distributions in the spinel and pentlandite

TABLE 1. Observed Distribution of Cations in Spinels and Pentlandites

Compound	Octahedral	Tetrahedral
$FeAl_2O_4$[a]	$2Al^{3+}$	Fe^{2+}
$CoAl_2O_4$[a]	$2Al^{3+}$	Co^{2+}
$NiAl_2O_4$[a]	$3/4Ni+5/4Al$	$1/4Ni+3/4Al$
$FeCr_2O_4$[a]	$2Cr^{3+}$	Fe^{2+}
$CoCr_2O_4$[a]	$2Cr^{3+}$	Co^{2+}
$NiCr_2O_4$[b]	Cr^{3+},Ni^{2+}	---
$FeCr_2S_4$[c]	$2Cr^{3+}$	Fe^{2+}
$CoCr_2S_4$[c]	$2Cr^{3+}$	Co^{2+}
$NiCr_2S_4$[d]	Cr^{3+},Ni^{2+}	---
$FeCo_2S_4$[e]	$2Co^{3+}(?)$	$Fe^{2+}(?)$
$CoCo_2S_4$[c]	$2Co^{3+}$	Co^{2+}
$NiCo_2S_4$[f]	$2Co^{3+}$	Ni^{2+}
$FeNi_2S_4$[c]	$Fe^{2+}+Ni^{3+}$	Ni^{3+}
$NiFe_2S_4$[c]	$Ni^{2+}+Fe^{3+}$	Fe^{3+}
$NiCo_8S_8$[g]	$Co+Ni$	$Co+Ni$
$(Fe,Ni)_9S_8$[h]	$3/4Fe+1/4Ni$	$Fe+Ni$

[a] Burns, 1970.
[b] Greenwood, 1970.
   (Spinel structure becomes pseudohexagonal)
[c] Vaughan et al., 1970.
[d] Andron and Bertant, 1966.
   (Spinel structure becomes pseudohexagonal)
[e] predicted.
[f] Knop et al., 1968.
[g] Knop and Ibrahim, 1961.
[h] Knop et al., 1970.

structures are listed in Table 1. In aluminum spinel, Ni^{2+} has a strong preference for the octahedral site. In chromium oxy- and thiospinels, both cations have a strong preference for the octahedral site and the structure distorts to become pseudohexagonal (Andron and Bertaut, 1966) with both Cr^{3+} and Ni^{2+} occupying octahedral sites. In $NiCo_2S_4$ and $FeNi_2S_4$, cobalt and iron occupy octahedral sites because they exist as low-spin ions in these structures and gain higher octahedral site preference energy than does Ni^{2+} (Vaughan *et al*, 1971). The ordering of iron in the octahedral site of natural pentlandite, as observed in the Mössbauer study, means that octahedral iron could be in the low-spin state in the pentlandite structure. Nevertheless, from the isomer shift of the same Mössbauer spectra, Knop *et al.* (1970) suggested that the octahedral iron is present only in the high-spin state. Although X-ray diffraction methods could not be used successfully to determine the distribution of iron and nickel in the two sites because of their similar X-ray scattering

factors, Rajamani and Prewitt (1973) predicted probable cation ordering from the observed interatomic distances in the pentlandite structure. The underlying assumption in their studies is that the interatomic distances are sensitive to the kind of cation, and to its valency, spin state, and coordination number. Table 2 provides such distances in the common sulfide structures. Consider, for example, iron in troilite and pyrite. The octahedral Fe-S distances in the two structures are 2.49 Å and 2.26 Å, respectively. It has been inferred from magnetic data that Fe^{2+} in troilite exists as a high-spin ion and in pyrite as a low-spin ion (Burns, 1970). The interatomic distances and the lattice parameter variations in the synthetic pentlandite series suggested that octahedral iron could be in the divalent high-spin state; however, evidence for significant ordering of Fe^{2+} (H·S) in the octahedral site was inconclusive. Therefore, the present investigation of the pentlandite structure at high temperature was undertaken to learn which changes in interatomic distances contribute to the thermal expansion. We also wanted to know whether the expansion is restricted only to iron-nickel pentlandite or is present in nat-

ural cobalt pentlandite as well. Thus, we examined the structures of two natural pentlandites—one containing essentially iron and nickel from Frood Mine, Sudbury, and another from Outokumpu, Finland containing 5.6 atoms of cobalt in the formula unit—at high temperatures (200°C for Frood and 235° and 350°C for Outokumpu) and at room temperature both before and after heating, using single-crystal X-ray intensity data.

Experimental Details

The crystals used in the present study were those used for room-temperature structure refinements by Rajamani and Prewitt (1973). The crystal data including composition, cell parameters and positional parameters are listed in Table 3.

The crystals were mounted with high-temperature cement on Suprasil silica glass fibers, placed inside silica glass capillaries, evacuated, and sealed. Before data collection the Frood pentlandite was heated at 200°C for 24 hours on the Picker diffractometer using the heating device described by Brown, Sueno, and Prewitt (1973). The procedure adopted for data collection was very similar to our previous studies (Rajamani and Prewitt, 1973). After completion of data collection at 200°C, the crystal was cooled to room temperature in approximately three hours and another set of data was collected at room temperature after heating. The Outokumpu pentlandite did not show significant expansion at 235°C and, therefore, one more set of intensity data was collected at 350°C in addition to the 235°C and the final room-temperature sets of data. The cell parameters at various temperatures for the two pentlandites were determined from the measured 2θ values using the PODEX 2 Program (Table 4). Long-exposure (220 hours) precession photographs of

TABLE 2. Interatomic Distances in Important Sulfide Structures

Structure Type	Minerals	Octahedral Bond Distance (Å)	Tetrahedral Bond Distance (Å)
Pyrite	[a]Pyrite, FeS_2	2.26	---
	[a]Cattierite, CoS_2	2.32	---
	[a]Vaesite, NiS_2	2.40	---
Spinel	[b]Greigite, Fe_3S_4	2.47	2.14
	[c]Linnaeite, Co_3S_4	2.25	2.19
	[c]Polydymite, Ni_3S_4	2.28	2.22
NiAs	[d]Troilite, FeS	2.49	---
	[e]Jaipurite, CoS	2.34	---
	[f]β-NiS	2.394	---
Pentlandite	[g]Synthetic Co_9S_8	2.36	2.20
	[h]Outokumpu Pn	2.373	2.209
	[h]Frood Pn	2.377	2.228
Heazlewoodite	[i]Ni_3S_2	---	2.28
Mackinawite	[j]$Fe_{1+x}S$	---	2.244

[a]Elliott, 1960.
[b]Skinner et al., 1964.
[c]Calculated.
[d]Evans, 1970.
[e]Kuznetsov et al., 1965.
[f]Trahan et al., 1970.
[g]Rajamani and Prewitt (unpublished).
[h]Rajamani and Prewitt, 1973.
[i]Fleet, 1972.
[j]Taylor and Finger, 1971.

TABLE 3. Room-Temperature Crystal Data on Pentlandites (Rajamani and Prewitt, 1973)

		Frood Pentlandite	Outokumpu Pentlandite
Composition		$Fe_{3.97}Ni_{4.84}Co_{0.07}S_8$	$Fe_{1.60}Co_{5.60}Ni_{1.82}S_8$
Cell Parameter a		10.038Å	9.977Å
Positional Parameter	4b	1/2,1/2,1/2	1/2,1/2,1,
	32f	0.1261	0.1262
	8c	1/4,1/4,1/4	1/4,1/4,1/4
	24e	0.2632	0.2623

TABLE 4. Cell Parameters and Thermal Expansion*

	24°C	200°C	235°C	350°C	24°C**	% Expansion (200°C)
Frood Pn	10.038(1)	10.158(1)	---	---	10.093(1)	1.2
Outokumpu Pn	9.977(1)	---	10.004(1)	10.031(1)	9.969(1)	0.27

Numbers in parentheses represent calculated standard errors (1σ̂) and refer to the last decimal quoted.

**Final room temperature after heating.*

both crystals were taken before and after heating to check the space group and the presence of any "foreign" phases.

Because the linear absorption coefficients were respectively 169 cm⁻¹ and 180 cm⁻¹ for the Frood and Outokumpu specimens, absorption corrections were applied to all sets of data using the method of Wuensch and Prewitt (1965), even though the maximum crystal dimension was slightly less than 0.1 mm. The resulting transmission factors varied between 0.29 and 0.35 for the Frood crystal and between 0.28 and 0.43 for the Outokumpu crystal. The absorption-corrected, observed structure factors of the symmetry-equivalent reflections were averaged in all cases with a total of approximately 100 reflections used for each refinement.

The refinement of the structures was carried out as described in our previous studies on pentlandites. Attempts were made to refine the occupancy of iron and nickel in the two crystallographically distinct metal sites of the Frood pentlandite. Three possible cation distribution schemes were considered: (a) slight ordering of iron in the tetrahedral sites, (b) slight ordering of iron in the octahedral site, and (c) complete random distribution of iron and nickel in the two metal sites. All three models gave approximately similar results, judging from R factors, temperature factors for individual atoms, and errors. The random distribution model was assumed in the final anisotropic refinements. Because Outokumpu pentlandite contains three cations which all have similar X-ray scattering factors, no attempt was made in the present study to refine the occupancy after annealing. Interatomic distances, bond angles, thermal ellipsoids and their associated errors were calculated using L. W. Finger's ERROR Program. Final positional parameters, isotropic temperature factors and R factors are tabulated in Tables 5a and 5b. Interatomic distances, angles,

and thermal ellipsoids for both pentlandites are listed in Tables 6, 7, and 8, respectively.

Results and Discussion

As can be seen in Table 4, the cell edge of Frood pentlandite at room temperature increased significantly after annealing from 10.038 Å to 10.093 Å. The magnitude of the expansion is in good agreement with that observed by Knop *et al* (1965, p. 310) for powdered samples of natural pentlandite. Though the cell edge of Outokumpu also increased with increasing temperature, the final room temperature a after annealing is slightly smaller than the initial room-temperature value. When a comparison is made between the two pentlandites, it is apparent that Frood pentlandite expanded at least 4 times as much as Outokumpu pentlandite (1.2 and 0.27 per-

TABLE 5a. Positional and Thermal Parameters in Frood Pentlandite*

		Initial Room Temperature	200°C	Final Room Temp. (after heating)
4b – M(0)	B	0.55(4)	1.37(4)	0.77(4)
32f – M(T)	x	0.12608(4)	0.12650(5)	0.12632(4)
	y	0.12608(4)	0.12650(5)	0.12632(4)
	z	0.12608(4)	0.12650(5)	0.12632(4)
	**β_{11}	0.00106(9)	0.00291(6)	0.00184(5)
	β_{12}	0.00008(4)	0.00010(4)	0.00008(3)
	Beq.	0.42(3)	1.20(2)	0.75(2)
8c = S1	B	0.58(4)	1.31(6)	0.83
24e = S2	x	0.2632(1)	0.2598(2)	0.2604(2)
	***β_{11}	0.0009(1)	0.0023(1)	0.0015(1)
	β_{22}	0.0011(1)	0.0030(1)	0.0019(1)
	Beq.	0.42	1.13(3)	0.73(3)
	†R	0.027	0.031	0.025
	††R(wt)	0.030	0.028	0.026
Extinction Correction		5 x 10⁻⁷	8 x 10⁻⁷	4 x 10⁻⁷

Errors in parentheses are one standard deviation.

**$\beta_{11} = \beta_{22} = \beta_{33}$; $\beta_{12} = \beta_{13} = \beta_{23}$.*

***$\beta_{22} = \beta_{33}$; $\beta_{12} = \beta_{13} = \beta_{23} = 0$.*

†$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

††$R(wt) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

TABLE 5b. Positional and Thermal Parameters in Outokumpu Pentlandite*

		Initial Room Temperature	235°C	350°C	Final Room Temp. (after heating)
4b = M(0)	B	0.55(3)	1.01(4)	1.24(4)	0.66(3)
32f = M(T)	x	0.12617(2)	0.12626(4)	0.12639(5)	0.12615(3)
	y	0.12617(2)	0.12626(4)	0.12639(5)	0.12615(3)
	z	0.12617(2)	0.12626(4)	0.12639(5)	0.12615(3)
	**β_{11}	0.00124(4)	0.00226(4)	0.00300(6)	0.00140(4)
	β_{13}	0.00006(2)	0.00010(3)	0.00015(4)	0.00011(2)
	Beq.	0.49(2)	0.91(2)	1.19(2)	0.56(2)
8c' = S1	B	0.62(3)	1.15(5)	1.41(7)	0.76(4)
24e = S2	x	0.2623(1)	0.2622(2)	0.2618(2)	0.2624
	***β_{11}	0.00093(8)	0.0020(1)	0.0022(2)	0.0014(1)
	β_{22}	0.00138(6)	0.0022(1)	0.0029(1)	0.0014(1)
	Beq.	0.49(2)	0.85(3)	1.08(3)	0.56
	†R	0.018	0.024	0.033	0.019
	††R(wt)	0.021	0.021	0.024	0.017
Extinction Correction		4×10^{-7}	3×10^{-7}	4×10^{-7}	4×10^{-7}

* *Errors in parentheses are one standard deviation.*

** $\beta_{11} = \beta_{22} = \beta_{33}; \quad \beta_{12} = \beta_{13} = \beta_{23}$

*** $\beta_{22} = \beta_{33}; \quad \beta_{12} = \beta_{13} = \beta_{23} = 0.$

† $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|.$

†† $R(wt) = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}.$

TABLE 6. Interatomic Distances (Å) in Pentlandites*

	Frood Pentlandite			Outokumpu Pentlandite			
Atoms	24°C	200°C	24°C**	24°C	235°C	350°C	24°C**
M(0)-S2[6]***	2.377(2)	2.440(2)	2.418(2)	2.373(1)	2.379(2)	2.389(2)	2.369(2)
M(T)-S1[1]	2.154(1)	2.173(1)	2.162(1)	2.140(1)	2.144(1)	2.148(1)	2.138(1)
M-(T)-S2[3]	2.258(1)	2.266(1)	2.255(1)	2.239(1)	2.245(1)	2.250(1)	2.238(1)
Mean M(T)-S	2.232	2.243	2.232	2.214	2.220	2.225	2.213(1)
M(T)-M(T)[3]	2.531(1)	2.570(1)	2.550(1)	2.518(1)	2.526(1)	2.536(1)	2.515(1)
M(T)-M(T)[3]	3.518(1)	3.548(1)	3.531(1)	3.494(1)	3.501(1)	3.507(1)	3.492(1)
S2-S2[4]	3.362(2)	3.451(3)	3.419(2)	3.355(1)	3.364(2)	3.379(3)	3.350(2)

* *The numbers in parentheses represent estimated standard errors (1σ) and refer to the last decimal place.*

** *At room temperature after heating.*

*** *The numbers in brackets refer to the multiplicity of the bond.*

TABLE 7. Important Bond Angles (°) in Pentlandites*

	Frood Pentlandite			Outokumpu Pentlandite			
	$24^{\circ}C$	$200^{\circ}C$	$24^{\circ}C$**	$24^{\circ}C$	$235^{\circ}C$	$350^{\circ}C$	$24^{\circ}C$**
S2-M(0)-S2	90.0	90.0	90.0	90.0	90.0	90.0	90.0
S1-M(T)-S2	107.18(4)	108.05(4)	107.84(4)	107.42(3)	107.45(3)	107.58(4)	108.05(4)
S2-M(T)-S2	111.66(4)	110.86(4)	111.06(4)	111.45(2)	111.42(3)	111.29(4)	110.86(4)
M(T)-M(T)-M(T)	90.0	90.0	90.0	90.0	90.0	90.0	90.0
M(T)-S1-M(T)	109.47	109.47	109.47	109.47	109.47	109.47	109.47
M(T)-S2-M(T)	68.19(4)	69.08(4)	68.87(4)	68.44(3)	68.47(4)	68.61(4)	69.08(4)
M(T)-S2-M(0)	127.55(4)	126.09(4)	126.90(4)	127.32(3)	127.29(3)	127.15(4)	126.69(4)

*
The numbers in parentheses represent estimated standard errors ($1\hat{\sigma}$) and refer to the last decimal place.
**
At room temperature after heating.

cent, respectively, for the two pentlandites) in the temperature interval 24° to 200°C.

The mean thermal expansion coefficient, α, which is expressed by the formula $(1/V_0)[(V_T - V_0)/(T - T_0)]$, where V_0 is the volume at a reference temperature T_0, is given for pentlandites and other sulfides in Table 9. The thermal expansion coefficient of the Outokumpu pentlandite is slightly larger than that of pyrite (although published values for pyrite vary considerably) and significantly smaller than that of pyrrhotite. However, in the case of Frood pentlandite, α is at least seven times as large as that

TABLE 8. Magnitudes and Orientations of Thermal Ellipsoids in Pentlandites*

		M(T)				S2			
Frood Pn	i of r_i	r_i	a	b	c	r_i	a	b	c
$24^{\circ}C$	1	0.070(2)	114	114	35	0.067(5)	0	90	90
	2	0.070(2)	66	66	145	0.075(2)	90	90	180
	3	0.079(2)	55	55	55	0.075(2)	90	90	0
$200^{\circ}C$	1	0.121(1)	114	114	35	0.109(4)	0	90	90
	2	0.121(1)	66	66	145	0.124(2)	90	90	180
	3	0.127(2)	55	55	55	0.125(2)	90	90	0
$24^{\circ}C$ (after heating)	1	0.096(2)	114	114	35	0.087(4)	0	90	90
	2	0.096(2)	66	66	145	0.100(3)	90	90	180
	3	0.101(1)	55	55	55	0.100(3)	90	90	0
Outokumpu Pn									
$24^{\circ}C$	1	0.077(1)	114	114	35	0.069(3)	0	90	90
	2	0.077(1)	65	65	144	0.083(2)	90	90	180
	3	0.082(1)	55	55	55	0.083(2)	90	90	0
$235^{\circ}C$	1	0.105(4)	114	114	35	0.100(4)	0	90	90
	2	0.105(4)	114	114	35	0.105(2)	90	90	180
	3	0.112(2)	55	55	55	0.106(2)	90	90	0
$350^{\circ}C$	1	0.120(1)	114	114	35	0.106(4)	0	90	90
	2	0.120(1)	114	114	35	0.122(2)	90	90	180
	3	0.129(2)	55	55	55	0.123(2)	90	90	0
$24^{\circ}C$ (after heating)	1	0.081(1)	114	114	35	0.084(3)	0	90	90
	2	0.081(1)	66	66	144	0.084(1)	90	90	180
	3	0.090(2)	55	55	55	0.084(1)	90	90	0

*
Numbers in parentheses are estimated standard errors referring to the last decimal place.

TABLE 9.   Thermal Volume Expansion of Certain Sulfide Minerals

Mineral		Coefficient of Expansion $\alpha \times 10^{-5}$ deg^{-1}	Mineral		Coefficient of Expansion $\alpha \times 10^{-5}$ deg^{-1}
Pyrite	[a](20-100°C)	2.1	Outokumpu Pentlandite	(24-235°C)	3.9
	[b](20-200°C)	2.9		(24-350°C)	5.8
	[c](20-300°C)	1.1			
			Frood Pentlandite	(24-200°C)	20.6
				*(24-200°C)	11.1
Pyrrhotite	[c](25-140°C)	4.5			
	[c]FeS(140-320°C)	12.5	Synthetic Pentlandite	[d](25-220°C)	15.1
	[c]Fe$_{.923}$S(75-320°C)	12.6			
	[c]Fe$_{.875}$S(25-292°C)	9.0			

[a]*Povarennykh, 1964.*

[b]*Skinner, 1966.*

[c]*Taylor, 1970.*

[d]*Morimoto and Kullerud, 1965.*

Reversible component of expansion.

of pyrite (where octahedral iron is present in the divalent low-spin state) and at least two times as large as that of pyrrhotite (where octahedral iron is present in the divalent high-spin state). Even in synthetic pentlandite α is larger than for pyrrhotite, the thermal expansion of which is a function of both composition and temperature interval (Taylor, 1970). Lack of data on individual polyhedral expansion in pyrite and pyrrhotite preclude comparison of the details of the thermal expansion of pentlandites with those of pyrite and pyrrhotite.

The refinement indicates that the structures of both pentlandites remained essentially the same at high temperature and at room temperature after heating. Only the positional parameter of the sulfur atom in 24e (S2) changed significantly at higher temperature. In the Outokumpu pentlandite, initial and final room-temperature refinement of the structure resulted in the same positional parameter for S2 in 24e. However, for Frood pentlandite, this parameter has significantly decreased after heating (from $x = 0.2632$ to $x = 0.2604$). Also, at 200°C, the change in x of S2 in Frood pentlandite is considerably larger than in Outokumpu pentlandite. The

geometries of the sulfur octahedra and tetrahedra did not change in either pentlandite due to heating. In the Outokumpu pentlandite, the $M(O)$-S distance and the $M(T)$-S distance increase with increasing temperature. Final room-temperature bond distances were essentially similar to those obtained before heating except for a small contraction (0.004 Å) in the $M(O)$-S distance. In the Frood pentlandite, the metal-sulfur distances also increased at 200°C as in Outokumpu. It should be noted that the octahedron in the Frood pentlandite expanded as much as ten times more than that in Outokumpu pentlandite in approximately the same temperature interval. Within the Frood pentlandite itself, the increase in $M(O)$-S distance is much larger than the $M(T)$-S distance. After heating, the octahedron showed a significant "irreversible" (with respect to cooling time used in our experiments) expansion (from 2.377 to 2.418 Å) whereas the tetrahedron did not show such expansion (as can be seen from the mean $M(T)$-S distance, 2.232 Å before and after heating.) $M(T)$-$M(T)$ distances also increased significantly as a result of heating.

The isotropic temperature factors are all in good

agreement with previously published values for other sulfide structures (Hall and Stewart, 1973; Rajamani and Prewitt, 1973). Also, the general relation between the coordination number of atoms and their temperature factors (*i.e.,* the higher the CN of the anion the smaller the temperature factor and *vice-versa* for cations) was observed in both pentlandites at all temperatures. In the pentlandite structure, only atoms in equipoints 32f and 24e could be anisotropic (a requirement arising out of the point symmetries of atomic positions). In the Frood pentlandite the r.m.s. amplitudes listed in Table 8 show that both these atoms are slightly anisotropic. In the case of Outokumpu pentlandite, the S2 atom became almost isotropic after heating. It is interesting to note that the equivalent isotropic temperature factors for both metal atoms and sulfur atoms in the Outokumpu pentlandite increased to the same extent in the temperature interval studied.

Thermal Expansion

It appears from the thermal expansion of Frood and Outokumpu pentlandites that the "irreversible" expansion is restricted only to iron-nickel pentlandite. This is not unexpected because the *a* values of cobalt-rich pentlandites were found to be very close to those of the corresponding synthetic compositions (Knop *et al,* 1965, p. 308). If we compare the reversible component (*i.e.,* that which is recovered on cooling in our experiments) of the expansion in the two pentlandites, Frood pentlandite showed two to three times as much increase as did Outokumpu pentlandite. This difference is particularly surprising when we consider the similarities of the two structures. Therefore, we suggest that the mechanisms of thermal expansion in the two structures are different because of the difference in the nature of cations involved in the structure.

The absence of diffraction spots other than those of pentlandite in the precession photographs exposed for 220 hours before and after heating indicates that for the crystals studied, no admixed phases were present in any substantial amount that might have dissolved due to heating, causing an expansion of the cell. Further, there appear to be no major structural changes responsible for the expansion. All this evidence leads us to assume that the 'irreversible" expansion observed in the Frood pentlandite may be due to order-disorder processes taking place between the metal sites in the structure. As mentioned earlier, Mössbauer studies on natural

pentlandite before and after annealing also revealed an order-disorder process in iron-nickel pentlandite. However, the possibility that the thermal expansion could be due to changes in the magnetic properties should be kept open.

Let us consider the change in the $M(O)$-S distance in the Frood pentlandite after heating. This change (0.041 Å) is very significant when we consider the differences in the octahedral interatomic distances between Ni-S and Fe(H·S)-S or Fe(L·S)-S in sulfide structures (Table 2). One possible way of expanding the $M(O)S_6$ octahedron is by increasing its occupancy by a larger cation. The problem encountered in the pentlandite structure is the determination of valency and spin state of octahedral iron. From the room-temperature interatomic distances in the Frood pentlandite (before annealing), it was not possible to predict the nature of octahedral iron with confidence because the occupancy of iron in the octahedral site was not known. However, from the Mössbauer spectra of natural pentlandite, Knop *et al* (1970) suggested that the octahedral iron is divalent, high-spin. Also, the variation of the cell edge with composition (in terms of iron and nickel content) as observed by Knop *et al* (1965), Shewman and Clark (1971), and Misra and Fleet (1973) indicates that in the pentlandite structure iron occupies a larger volume than does nickel; therefore, octahedral iron probably is in the divalent high-spin state. If the process of cation order-disorder between cation sites alone were responsible for the irreversible thermal expansion, then we predict from the observed increase in the $M(O)$-S distance that annealing resulted in the enrichment of $Fe^{2+}(H·S)$ in the octahedral site of the Frood pentlandite. Alternatively, Ni^{2+} would have been enriched in the octahedral site before annealing. Though our interpretation of the cation ordering in the Frood pentlandite is at variance with the suggestion made by Knop *et al* (1970), it is consistent with the chemistry and bonding aspects of natural pentlandite. As discussed elsewhere (Rajamani and Prewitt, 1973), the 8 tetrahedral metal atoms in the formula unit form a cube cluster in which the number of 3d electrons is fixed. In nickel-rich pentlandites, this number will exceed the constant value of 56 electrons because nickel has eight 3d electrons. Ordering of nickel in the octahedral site, in addition to creation of tetrahedral cation vacancies, could possibly reduce the number of 3d electrons to the constant value. Also, if the octa-

hedral iron is in the divalent high-spin state in the pentlandite structure, then Ni^{2+} will have higher octahedral-site-preference energy and, therefore, it is not unreasonable to expect nickel to order in the $M(O)$ site.

Contrary to what one might expect from the expansion of the octahedra, the tetrahedral interatomic distances in the Frood pentlandite did not show any change after heating. There may be two reasons for this: (1) In the pentlandite structure, the ratio of occupied octahedral to tetrahedral sites is 1:8 for the ideal stoichiometric composition. Therefore, whereas a small change in the occupancy of iron and nickel in the octahedral site would cause a significant change in the octahedral interatomic distance, such a small change may not cause an observable change in the tetrahedral interatomic distance. The amount of nickel transferred from octahedral to tetrahedral sites (due to disordering) would be very small, and even this small amount of nickel would be distributed in eight tetrahedral sites. This is illustrated graphically in Figure 1. Here the interatomic distances for octahedra and tetrahedra are plotted versus an occupancy parameter, p, where p is defined in the following way:

	Fe	Ni
octahedral site (4b)	p	$1-p$
tetrahedral site (32f)	$Fe_{tot} - p$	$Ni_{tot} - (1-p)$

(2) The lattice parameter variations in pentlandite as observed by Knop and Ibrahim (1961, p. 308), Knop et al (1965), and Misra and Fleet (1973) show that a becomes insensitive to nickel content for nickel-rich compositions of pentlandites. Because nickel would necessarily have to go into the tetrahedral sites when pentlandite becomes nickel-rich (i.e., Ni:Fe > 1), the above observation suggests that small changes in the occupancy of iron and nickel in the $M(T)$ sites do not cause significant expansion of the $M(T)$ sites.

The interpretation of order-disorder in the Frood pentlandite to explain the "irreversible" thermal expansion is based solely on the observed changes in the interatomic distances after heating. If the octahedral iron in natural pentlandite were in the low-spin state, then the possibility exists that there could be irreversible spin transition (low-spin to high-spin) which might be responsible for the octahedral expansion and, therefore, cell expansion. Although the Mössbauer studies did not indicate this possibility, a detailed magnetic study of natural
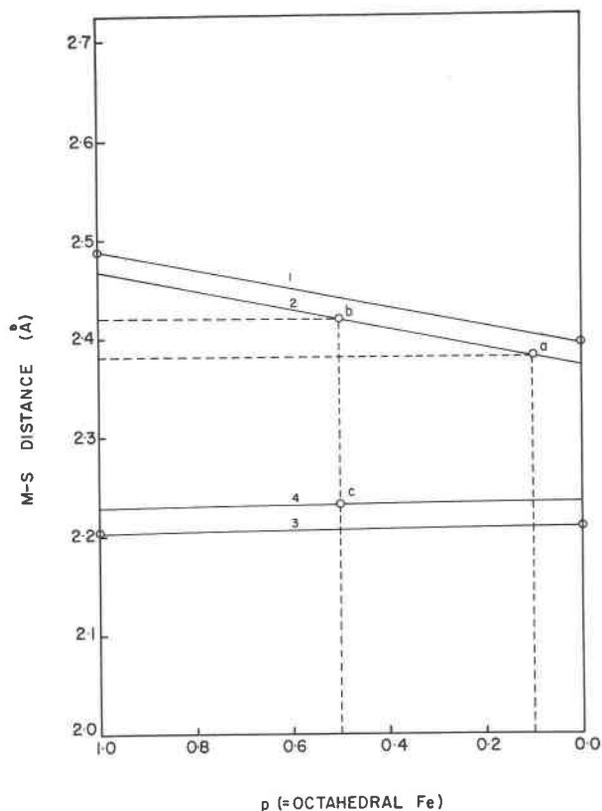
FIG. 1. Variation of interatomic distances as a function of an occupancy parameter, p, as defined in the text. (1) ^{VI}M-S distance when S is in sixfold coordination. (2) ^{VI}M-S distance in pentlandite (points a and b correspond to the distances in Frood pentlandite before and after heating, respectively). (3) Expected variation in ^{IV}M-S distance, calculated on the basis of the observed tetrahedral distances in the spinel structure for Ni and in mackinawite for Fe. (4) Observed ^{IV}M-S distance in pentlandite (point c corresponds to the distance before and after heating in the Frood Pn).

pentlandite before and after annealing is needed to completely resolve this problem. Because the Outokumpu pentlandite containing 5.6 atoms of cobalt in the formula unit did not show irreversible expansion, it would be instructive to study the thermal expansion behavior of natural pentlandite containing a smaller amount of cobalt. Also, because in argentian pentlandite $(Fe, Ni)_8 AgS_8$ the octahedral site is almost completely filled with silver and the tetrahedral sites contain essentially iron and nickel (Hall and Stewart, 1973), annealing experiments on this mineral would give further useful information on the problem of thermal expansion of pentlandite.

Acknowledgments

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